Influence of Hydrocarbon Chain Length in Phenyl(Alkyl)trimethoxysilane Inhibitors on AS-ALD Selectivity: Comparison of Gas-phase and Liquid-phase Adsorption

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Area-selective atomic layer deposition (AS-ALD) has become a critical technique for precise material fabrication, particularly in complex nanoarchitectures. Achieving high selectivity in AS-ALD requires the strategic use of effective small molecular inhibitors (SMIs) to prevent undesired growth on non-target surfaces[1,2]. In this study, we investigated how variations in the hydrocarbon chain length (n = 1–6) of Phenyl(Alkyl)trimethoxysilane inhibitors influence their adsorption and precursor-blocking performance during the AS-ALD of vanadium dioxide (VO_2). To analyze the adsorption characteristics, we employed two different adsorption methods: (1) liquid-phase adsorption via spin-coating and (2) gas-phase adsorption by supplying vaporized SMIs into the chamber. The SMI-coated SiO_2 surfaces formed through liquid-phase adsorption exhibited highly similar characteristics, with water contact angle (WCA) variations within 5° among different SMIs. Furthermore, after 100 ALD cycles of VO_2 deposition, all samples demonstrated high selectivity above 90%, regardless of the SMI used. However, in the gas-phase adsorption process, significant differences were observed depending on the chain length. The WCA varied by more than 20°, indicating substantial surface property differences. Additionally, after 100 cycles, selectivity ranged from a maximum of 89.9% (n = 2) to a minimum of 4.5% (n = 6), revealing a significant disparity in selectivity. To elucidate these differences, we employed density functional theory calculations and random sequential adsorption simulations[3]. Experimental validation was conducted using WCA, X-ray photoelectron spectroscopy, X-ray fluorescence, and scanning electron microscopy. These findings highlight the importance of appropriate molecular characteristics and structures depending on the adsorption method and underscore the necessity of tailored molecular design to achieve optimal AS-ALD performance.

Reference

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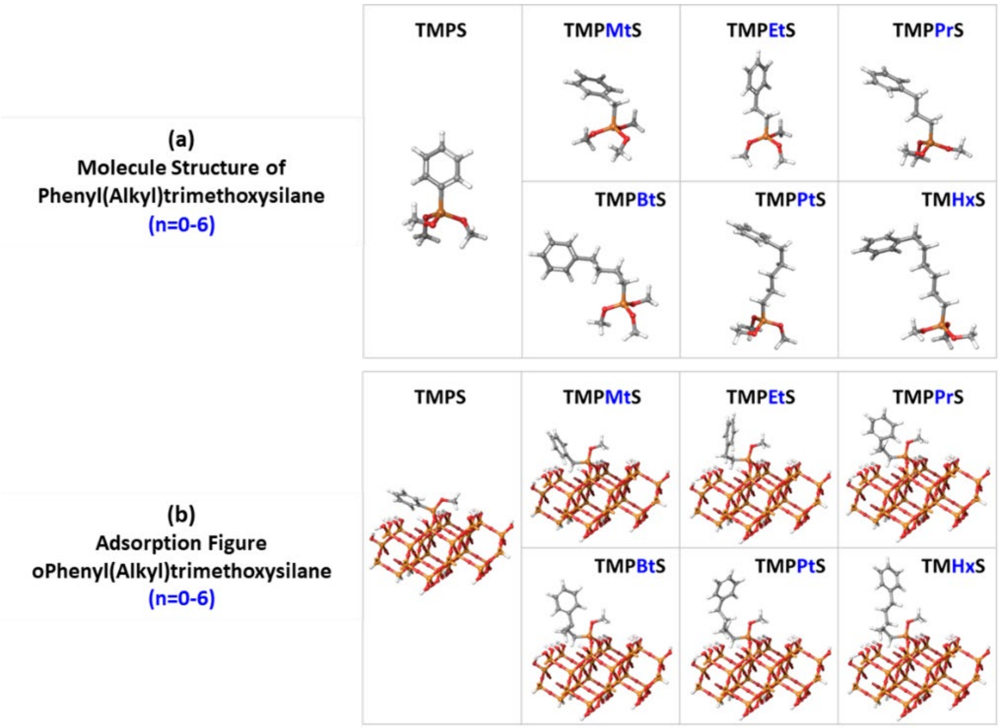

Fig. 1. (a) Molecular structures of Phenyl(Alkyl)trimethoxysilane (n = 0–6), including TMPS, TMPMtS, TMPEtS, TMPPrS, TMPBtS, TMPPtS, and TMHxS. The structures highlight the variation in hydrocarbon chain length, ranging from methyl to hexyl groups.(b) Adsorption configurations of Phenyl(Alkyl)trimethoxysilane molecules (n = 0–6) on SiO_2 surfaces, demonstrating the differences in molecular orientation and adsorption behavior with increasing chain length.

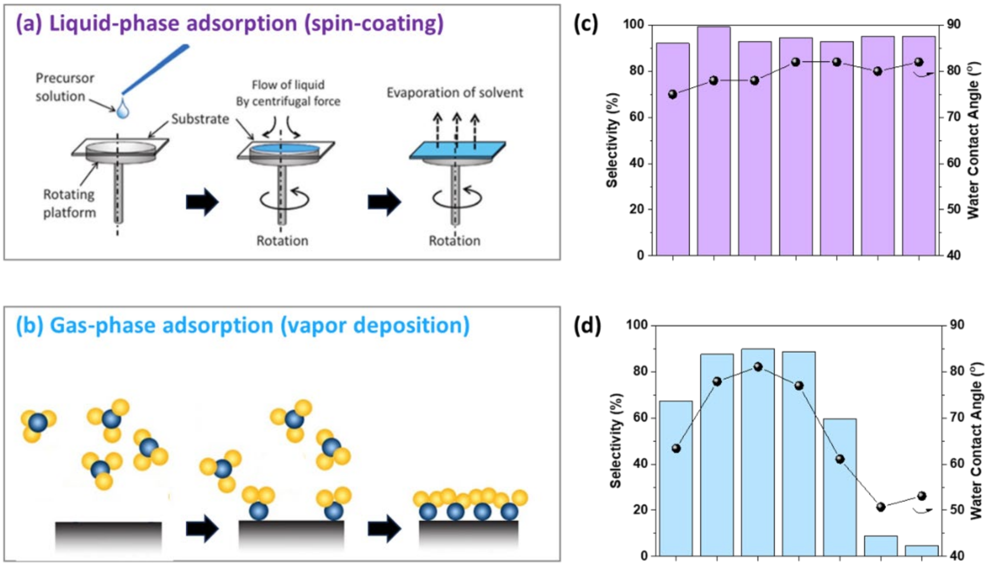

Fig. 2. (a-b) Schematic illustrations of (a) liquid-phase adsorption (spin-coating) and (b) gas-phase adsorption (vapor deposition). (c-d) Plots showing selectivity (%) and water contact angle (°) for (c) liquid-phase adsorption, which exhibits consistent selectivity and minimal water contact angle variation, and (d) gas-phase adsorption, which demonstrates significant variations in both selectivity and water contact angle depending on the SMI chain length.